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INKJET RECORDING PAPER  
[Inkujetto kiroku yoshi]

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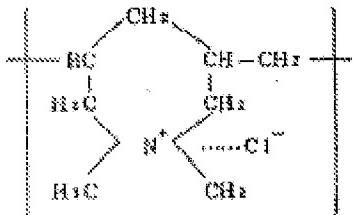
APPLICANT (71): Jujo Paper Co. Ltd.

TITLE (54): INKJET RECORDING PAPER

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## Claims

1. An inkjet recording paper composed by applying or infiltrating a mixture of a dimethyl diallyl ammonium chloride polymer, having a monomer with the following structural formula as the component unit, and a polyethyleneimine into a base.



2. The inkjet recording paper according to Claim 1, characterized by the fact that the solid part compounding ratio of the dimethyl diallyl ammonium chloride polymer and the polyethyleneimine in the aforementioned mixture is 95-50 to 5-50.

## Detailed explanation of the invention

The present invention concerns an inkjet recording paper wherein the recording image has complete water resistance and even the light resistance is excellent.

Generally, inkjet recording is a system of carrying out dot recording on a recording paper from a distance of a few millimeters or a few tens of millimeters, with the ink granules formed by pressurizing and jetting ink from a fine hole having a diameter of a few tens of microns. Therefore, a water-based ink of low viscosity and high surface resiliency is normally used. When trying to secure jetting of ink from the fine hole, it is difficult to include pigments, resins, and the like as is done in regular printing ink. Therefore, the recording quality such as the recording resolution, concentration, gloss, light resistance, water resistance, and the like in inkjet recording is naturally inferior to that of general printing.

However, the quality demanded by the customers in inkjet recorded materials have become more stringent with expansion in the field of use of inkjet recording systems, and there is an increased trend

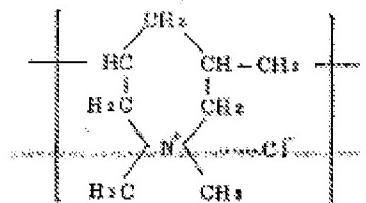
toward requiring light resistance and water resistance in the recorded materials in addition to the recording resolution, concentration, vivid color tones, and the like. When presenting material outdoors that was printed by inkjet recording, the recording bleeds and the color fades just by storing the recorded printed matter in a high-humidity environment, and this tendency is found extensively in color inkjet printed materials.

Ink for inkjet recording is composed from water-soluble dyes, which are generally classified into direct dyes, acidic dyes, and basic dyes, water, dye solubilizing agent, wetting agent, etc., and colors other than black are toned by mixing one or more kinds selected from among three components of yellow, magenta, and cyan. The method of adding a waterproofing agent directly into the ink to waterproof the printed materials can also be considered. However, this method has a problem from the standpoint of the aforementioned ink composition and preventing clogging of the ink.

The present inventor proposed the use of a dimethyl diallyl ammonium chloride polymer in order to make the recorded images water-resistant in Japanese Patent Application No. Sho 57[1982]-130270 and demonstrated that when this dimethyl diallyl ammonium chloride polymer is applied or infiltrated into the base, a considerable water resistance is manifested not only in black recorded images but even in color recorded images.

However, the recording paper related to this proposal was not sufficient regarding the light resistance of the recording paper, and there was still room for improvement. As a result of further examination in order to solve these problems, the present inventors found that the aforementioned problems can be improved on by using a polyethyleneimine in combination. Namely, it was recognized that an inkjet recording paper obtained by applying or infiltrating a mixture of dimethyl diallyl ammonium chloride polymer and polyethyleneimine into the base manifests excellent qualities regarding not only the water resistance of recorded images but also the light resistance.

Below, the present invention will be explained in detail. The dimethyl diallyl ammonium chloride polymer used in the present invention is a polymer with a monomer with the following structural formula as the component unit.



This dimethyl diallyl ammonium chloride polymer is a hygroscopic white powder used as a conductive finishing agent and is characterized by the fact that it does not dissolve in any organic solvent except methanol, but dissolves well in water, and the aqueous solution thereof is very stable, whether it be acidic or alkaline.

On the other hand, polyethyleneimine is a strong cationic aqueous solution and is an example of a polycationic high polymer electrolyte proposed for use in Japanese Kokai Patent Application No. Sho 56[1981]-84992 to achieve water resistance of inkjet recording images. However, not much water resistance can be expected from this polyethyleneimine with regard to color recording images, not to mention black recording images. However, when polyethyleneimine is used in combination with dimethyl diallyl ammonium chloride polymer, there is a noticeable effect in improving the light resistance and the water resistance.

As the method of use of these mixtures in the present invention, it can be sprayed on the surface of a commonly known inkjet recording paper in the aqueous state, applied or infiltrated into the surface with a size press, a roll coater, or the like during the paper making process, or mixed into the coating material of a commonly known coated inkjet recording paper and applied with a coating apparatus such as a blade, an air knife, a roll coater, or the like.

The present invention can be applied to various types of inkjet recording papers and does not matter whether it is the plain type or the coated type and can obtain inkjet recording papers having a very high degree of color image water resistance and excellent light resistance of images by using in recording papers incorporated with various fillers such as talc, kaolin, calcium carbonate, urea formaline resin powder, or the like, and recording papers coated with a white pigment such as granular silica, acidic clay, clay, talc, calcium carbonate, silicious earth, titanium oxide, barium sulfate, or the like with a water-soluble high-polymer binder such as acidic starch, gelatin, casein, polyvinyl alcohol, cellulose derivatives, polyvinyl pyrrolidone, or the like.

Incidentally, there is no restriction in particular with regard to the compounding ratio of dimethyl diallyl ammonium chloride polymer and polyethyleneimine. However, it is preferable to be about 95-50 to 5-50 in solid part ratio, since the light resistance becomes insufficient if the ratio of the former is too low. An application amount or infiltrating amount of about  $0.1\text{-}2.5 \text{ g/m}^2$  manifests sufficient water resistance and light resistance for images.

Below, the present invention will be explained with reference to application examples.

### Application examples

An aqueous solution of 15 parts by weight (solid parts) of completely saponified polyvinyl alcohol (manufactured by Kuraray Co., Ltd. PVA117) as the binder and a mixture of 4 parts by weight (solid parts) of dimethyl diallyl ammonium chloride polymer (manufactured by Nitobo Co., Ltd., Pasu [transliteration] H-10) and polyethyleneimine (manufactured by Bateishiyu [transliteration] Senryo Kagakuhin Co., Ltd., Polymin P) of various compounding ratios were added to a slurry of 81 parts by weight (solid parts) of white carbon (manufactured by Tokuyama Soda Co., Ltd., Tokuseal U) as the pigment and prepared a series of coating materials of 15% solid part concentration based on the commonly

known recipe for coated inkjet recording paper. These coating materials were applied on a good quality marketed paper of paper weight in gsm 60 g/m<sup>2</sup>, stockhit size degree 20 sec with a wire bar so that the amount applied is 8-12 g/m<sup>2</sup>, they were then passed through a test calendering machine (manufactured by Yuriroll Co., Ltd.) once at linear pressure 24 kg to obtain inkjet recording papers No.1-No.6.

The light resistance test results of these recording papers are shown in Table 1 and Figure 1.

TABLE 1

④ 用 紙 №	比較例		実 施 例						比較例	
	№ 1	№ 2	№ 3	№ 4	№ 5	№ 6	№ 7	№ 8	№ 9	№ 10
⑤ 組 合	タメチルジアリルアンモニウムグリコライド混合物	100	80	60	40	30	0			
比 比	ギリエチレンイミン	6	20	40	60	80	100			
⑦ 平 常 黄 ( 種 )	201	167	189	182	179	189				
⑧ 照 射 時 間 ( 時 間 )	0 4 10	0 4 10	0 4 10	0 4 10	0 4 10	0 4 10	0 4 10	0 4 10	0 4 10	0 4 10
⑨ 色	ブ ラ ッ タ ⑩	0.79 0.75 0.72 0.76 0.77 0.73	0.84 0.83 0.80 0.83 0.81 0.77	0.72 0.74 0.76 0.74 0.76 0.74	0.71 0.73 0.74 0.74 0.74 0.71	0.70 0.72 0.71 0.71 0.71 0.70	0.71 0.72 0.71 0.71 0.71 0.71			
⑪	0.77 0.76 0.73 0.75 0.74 0.76	0.75 0.75 0.74 0.75 0.74 0.75	0.74 0.75 0.76 0.74 0.76 0.75	0.71 0.73 0.74 0.73 0.74 0.71	0.70 0.72 0.71 0.71 0.71 0.70	0.69 0.70 0.71 0.70 0.71 0.69	0.68 0.69 0.68 0.68 0.68 0.68			
⑫ 濃 度	マ ザ ナ ダ ⑪	0.83 0.77 0.72 0.80 0.76 0.69	0.78 0.77 0.86 0.84 0.81 0.74	0.82 0.81 0.86 0.82 0.81 0.77	0.81 0.82 0.87 0.85 0.85 0.81	0.80 0.81 0.82 0.81 0.81 0.80	0.79 0.80 0.81 0.80 0.80 0.79	0.78 0.79 0.78 0.78 0.78 0.78	0.77 0.78 0.77 0.77 0.77 0.77	0.76 0.77 0.76 0.76 0.76 0.76
⑬ イ エ ネ	0.49 0.49 0.49 0.50 0.51 0.50	0.52 0.51 0.51 0.52 0.51 0.51	0.51 0.51 0.52 0.51 0.51 0.51	0.49 0.48 0.47 0.47 0.47 0.46	0.48 0.47 0.52 0.51 0.51 0.49	0.47 0.46 0.51 0.49 0.49 0.48	0.46 0.45 0.44 0.44 0.44 0.43	0.45 0.44 0.43 0.43 0.43 0.42	0.44 0.43 0.42 0.42 0.42 0.41	0.43 0.42 0.41 0.41 0.41 0.40
合 計 ⑭	2.88 2.77 2.65 2.83 2.79 2.66	2.91 2.86 2.71 2.92 2.77 2.62	2.85 2.85 2.79 2.85 2.85 2.74	2.85 2.85 2.79 2.84 2.84 2.73	2.84 2.84 2.79 2.83 2.83 2.72	2.83 2.83 2.78 2.82 2.82 2.71	2.82 2.82 2.77 2.81 2.81 2.70	2.81 2.81 2.76 2.75 2.75 2.69	2.80 2.80 2.75 2.74 2.74 2.68	2.79 2.79 2.74 2.73 2.73 2.67
⑮ 露 色 差	— 3.8 3.0 — 1.4 6.0 —	1.7 6.9 — 5.1 10.3 —	8.5 14.2 — 13.9 18.1							

- Key:
- 1 Comparative Example
  - 2 Application Example
  - 3 Comparative Example
  - 4 Paper No.
  - 5 Compounding ratio

- 6 Dimethyl diallyl ammonium chloride polymer  
 Polyethyleneimine
- 7 Smoothness (sec)
- 8 Irradiation time (h)
- 9 Color density
- 10 Black
- 11 Cyan
- 12 Magenta
- 13 Yellow
- 14 Total
- 15 Fading rate

(1) Color density: The reflection density that was measured with a Macbeth densitometer by carrying out solid printing for four colors of black, cyan, magenta, and yellow using Inkjet Color Image Printer 10-0700 manufactured by Sharp and using the following SPI filters for the respective print section.

印刷部分の色	フィルターの種類
ブ ラ ッ タ	ブ ラ ッ タ 用 ビ ク ュ ア ル
シ ャ ッ タ	シ ャ ッ タ 用 レ フ ド
マ ゼ ッ タ	マ ゼ ッ タ 用 ダ リ ー ヴ
イ ョ ッ タ	イ ョ ッ タ 用 ブ ル ー

Key	1	Color of the print section
	2	Black
		Cyan
		Magenta
		Yellow
	3	Type of filter
	4	Visual for black
		Red for cyan
		Green for magenta
		Blue for yellow

(2) Irradiation time: Carbon arc irradiation time of feedometer

(3) Fading rate: Calculated with the following formula

$$\text{①} \quad \text{褪色率 (\%)} = \frac{\text{②} \text{ 照射前の反射濃度合計値} - \text{③} \text{ 照射後の反射濃度合計値}}{\text{④} \text{ 照射前の反射濃度合計値}} \times 100$$

Key:	1	Fading rate (%)
	2	Reflection concentration total value before irradiation
	3	Reflection concentration total value after irradiation
	4	Reflection concentration total value before irradiation

An effect of the fading being minimized when either the dimethyl diallyl ammonium chloride polymer or the polyethyleneimine is added to the other in comparison to using them independently is recognized from Table 1 and Figure 1. Incidentally, with regard to water resistance, fading was hardly recognized in any of the printed materials even when immersed for 24 h.

#### Brief description of the figures

Figure 1 is a graph that shows the fading rates of Table 1 in relation to the compounding ratio.

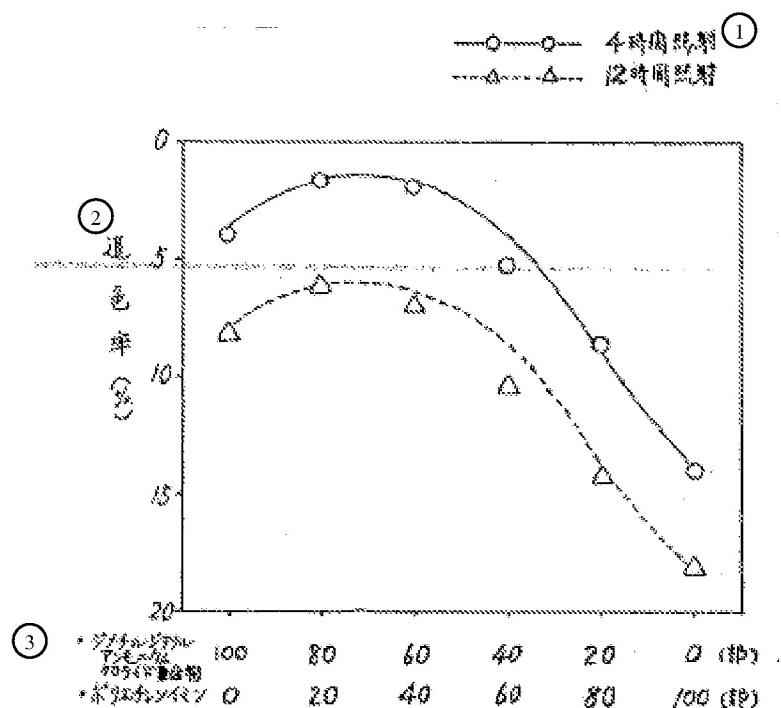


Figure 1

- Key 1 4 h of irradiation
- 12 h of irradiation
- 2 Fading rate (%)
- 3 • Dimethyl diallyl ammonium chloride polymer
- Polyethyleneimine